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Novel approach for the voltammetric evaluation of antioxidant activity using DPPH•-modified electrode

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ABSTRACT

The electrochemical behavior of 2,2-diphenyl-1-picrylhydrazyl (DPPH•) immobilized on the electrode surface has been studied. Bare glassy carbon electrode (GCE) and modified with dispersions of CeO_2 nanoparticles in water (CeO_2-H_2O/GCE) and cationic surfactant cetylpyridinium bromide medium (CeO_2-CPB/GCE) has been investigated as a platform for the DPPH• immobilization. The best voltammetric characteristics (peak potential separation of 70 mV, system reversibility with currents ratio of 0.98 and the highest peaks currents) have been observed on CeO_2-CPB/GCE. The effect of CeO_2 nanoparticles concentration has been evaluated. Scanning electron microscopy and electrochemical impedance spectroscopy have been applied for the electrode characterization. DPPH•/CeO_2-CPB/GCE has been used for the estimation of the antioxidants activity of natural phenolic antioxidants (quercetin, tannin, catechin and ferulic acid) expressed as the EC_{50} parameter according to differential pulse voltammetric (DPV) data. The EC_{50} decreased in the following order: quercetin (29 ± 1 μM), tannin (29 ± 4 μM), catechin (117 ± 4 μM) and ferulic acid (731 ± 17 μM). These data are in a good agreement with the results of standard spectrophotometric determination. The developed approach has been successfully applied for the antioxidant activity evaluation of medicinal herbs tinctures, infusions and decoctions.

1. Introduction

Free radical oxidation in living systems promoted by reactive oxygen and nitrogen species is considered as one of the reasons of aging and a wide range of pathological states like atherosclerosis, cancer, heart and neurodegenerative diseases and etc. [1–3]. The harmful effect of these processes is prevented or balanced by the antioxidant defense system consisting of the endogenous and exogenous antioxidants [4]. The last ones represented by a wide range of compounds of different classes contained in foodstuffs, bioactive additives and pharmaceuticals including medicinal herbs. The majority of low-molecular weight antioxidants act as the free radical traps breaking the propagation of the chain radical process [5]. Therefore, the evaluation of the antioxidant power of individual compounds and real samples of complex antioxidant composition is of interest.

One of the common parameters for the antioxidant properties characterization is the antioxidant activity based on the reactions with stable free radicals. Among then, DPPH• is the most frequently used standard radical. In this case, the antioxidant activity is expressed as a portion of the reduced radicals via the reaction with antioxidants of the sample or in the equivalents of the individual antioxidants, for instance, Trolox (commercial water-soluble vitamin E) [6,7]. Antioxidant activity for the individual compounds is usually expressed as the efficient concentration (EC_{50}), that is the amount of antioxidant necessary to decrease by 50% the initial DPPH• concentration [8].

Various methods of monitoring the amount of DPPH• in the antioxidant test systems have been reported including electron spin resonance spectroscopy [9], nuclear magnetic resonance [10] and spectrophotometry [8,11]. The last one became the most widely and commonly used approach due to its simplicity and cost-efficiency.

The reactions of the antioxidants with DPPH• is based on the electron transfer that allows the use of electrochemical methods for monitoring of this process. The number of the electroanalytical methods advantages like simplicity, high sensitivity, cost-efficiency and possibility of miniaturization and automatization makes them very attractive in antioxidant analysis [12,13] and could be applied for the DPPH-based antioxidant activity evaluation.

Several electrochemical approaches have been developed for the evaluation of the antioxidant capacity. All of them are based on the DPPH• reaction with antioxidants in solution with different

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